



## Applied Catalysis B: Environmental

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## Accelerated methylene blue (MB) degradation by Fenton reagent exposed to UV or VUV/UV light in an innovative micro photo-reactor

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## ARTICLE INFO

## Article history:

Received 5 November 2015

Received in revised form 4 January 2016

Accepted 9 January 2016

Available online 13 January 2016

## Keywords:

Vacuum-UV (VUV)

Photo-Fenton

Micro photo-reactor

Methylene blue

Oxidative radicals

Reaction mechanism

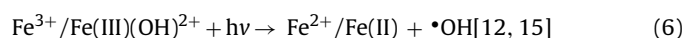
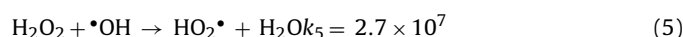
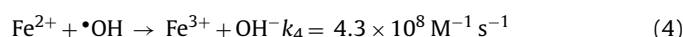
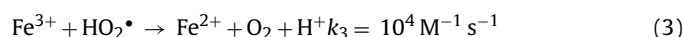
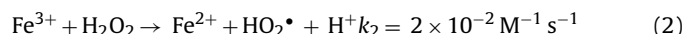
## ABSTRACT

This study presents the accelerated discoloration/degradation of methylene blue (MB) in solution by Fenton reagent under exposure to ultraviolet (UV) or Vacuum-UV/UV (VUV/UV) light in an innovative micro photo-reactor. The MB degradation was kinetically faster when using VUV/UV light at 254/185 nm compared to UV-irradiation at 254 nm. Oxidative radicals produced by the photo-Fenton process were identified with appropriate scavengers. The addition of benzoquinone (BQ) at millimolar (mM) concentrations to MB solutions precluded completely the MB photo-induced bleaching, while *tert*-butanol hindered to a lesser extent the MB degradation suggesting that HO<sub>2</sub><sup>•</sup> was the predominant intermediate leading to MB degradation. The VUV/UV micro photo-reactor comprised mercury resonance lines at 185 and 254 nm. The photon percentages absorbed by water were estimated to be 16.8% at 254 nm and 78.3% at 185 nm by water, while those absorbed by H<sub>2</sub>O<sub>2</sub> were 0.9% and 2.2%, correspondingly. The solution parameters affecting the features of MB degradation, such as MB, Fe, and H<sub>2</sub>O<sub>2</sub> concentrations, were explored and reaction mechanism was proposed. The lifetimes of <sup>•</sup>OH and HO<sub>2</sub><sup>•</sup> were estimated to be 2 ns and 0.38 s under an optimized solution with 0.016 mM MB, 0.147 mM H<sub>2</sub>O<sub>2</sub> and 0.05 mM Fe<sup>3+</sup>. Moreover, an estimation of the mean free paths of these radicals in solution provided the evidence that it was the radical lifetimes and mean-free paths, not their oxidation potentials that controlled the MB degradation kinetics. This study shows the potential of this VUV/UV assistant photo-Fenton process for the degradation of diluted organic compounds in aqueous solution.

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## 1. Introduction

In recent decades, several advanced oxidation processes (AOPs) that produce highly oxidative radicals such as <sup>•</sup>OH, <sup>•</sup>OH, Cl<sup>•</sup> have been reported and applied in water/wastewater treatments [1–10]. The Fenton/photo-Fenton process has been widely reported for the decontamination of a large range of recalcitrant and/or non-biodegradable pollutants during the treatment of industrial wastewaters [11–16]. Photo-Fenton studies deal with the process driven by UV or visible light irradiation generating oxidative radicals from Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub> [17–22]. The main reactions are shown below. The reaction H<sub>2</sub>O<sub>2</sub> + hv → 2<sup>•</sup>OH is not important due to the sub-millimolar (mM) H<sub>2</sub>O<sub>2</sub> concentration used

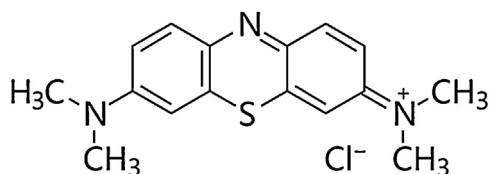


UV-light sources in photo-reactors commonly use the 254 nm low-pressure mercury emission line with a relative high photo-electric conversion efficiency of ~30% in the UV-range [23,24]. Low-pressure mercury lamps are able to generate mercury resonance lines at 254 nm and 185 nm. The percentage of 185 nm photons varies between 8% [25] and 25% [26] depending on the lamp power and manufacturer. These lamps use synthetic quartz of high purity allowing full transparency for the mercury resonance line at 185 nm [25,26].

The VUV generates radical and ions in water as reported by several laboratories [27–30]. VUV photolysis of pure liquid water leads to radicals <sup>•</sup>OH, HO<sub>2</sub><sup>•</sup>, O<sub>2</sub><sup>•-</sup>, H<sup>•</sup>, and stable species like H<sub>2</sub>O<sub>2</sub>,

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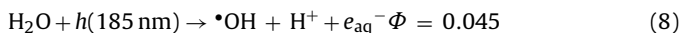
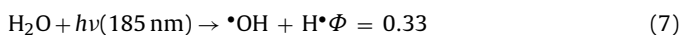
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Scheme 1. (MB).

$\text{HO}_2^-$ ,  $\text{O}_2$ . In this study the kinetics of photoreactions depends on the molar absorption coefficient of water and of methylene blue (MB) in the UV and VUV region. The degradation by  $\text{H}_2\text{O}_2$ /UV of 4-chlorophenol in a slurry photocatalytic reactor has been reported and the degradation study included modeling of the photocatalytic steps [31]. The degradation of pollutants using  $\text{H}_2\text{O}_2$ /UV has been reported using some modeling [32,33].

Even though the  $\text{H}_2\text{O}_2$ /UV process presents similarities with the VUV process, there are substantial differences: a in the  $\text{H}_2\text{O}_2$ /UV process, the photolysis of  $\text{H}_2\text{O}_2$  only generates  $\bullet\text{OH}$ , whereas in the VUV process, photolysis of water generates  $\bullet\text{OH}$ ,  $\text{H}^\bullet$  and  $e_{\text{aq}}^-$ , which modify the observed radical reactions. VUV is able to induce homolysis and ionization of  $\text{H}_2\text{O}$  at 185 nm, as shown below in Eqs. (7) and (8) [34,35], b  $\text{H}_2\text{O}_2$ /UV direct photolysis of many organic compounds can be neglected due to their low molar absorption coefficients since they absorb light  $< 200$  nm [3,4].



Therefore, the radicals noted by Eqs. (7) and (8) contribute to the oxidative radicals produced by the Fenton/photo-Fenton reagent shown above in Eqs. (1)–(6) leading to MB degradation. Scheme 1 shows the MB structural formula.

The sources of  $\bullet\text{OH}$  radicals by the Fenton reagent have been already noted in Eqs. (1), (6)–(8). But  $\text{H}_2\text{O}_2$  by itself as noted in Eqs. (7) and (8) is an additional sources of  $\bullet\text{OH}$ -radicals. Fig. 1 shows graphically the VUV 185/254 nm mercury lines compared to the UV254 nm mercury resonance line. The molar absorption coefficients of  $\text{H}_2\text{O}_2$  and  $\text{Fe(III)}$  increase towards shorter wavelengths molar absorption coefficients of  $\text{H}_2\text{O}_2$  are too low to absorb a significant amount of VUV/UV and UV light at the low molarities used in the photo-reactor. Work of our own group reported Fe-transitions in solution the microsecond region, depending on the

counter-ion, pH and Fe-species concentration [17]. The Fe (d-d) transition depend on the solution parameters and have been reported to occur within the nanosecond/microsecond range [4,36].

Recently, we have reported VUV micro photo-reactor (VMPR) for bench-scale experiments, with mercury resonance lines at 185/254 nm or alternatively presenting the mercury resonance line at 254 [37]. This precludes the very low transmittance in quasi-collimated photo-reactors in air, due to the short penetration of VUV light in air of  $\sim 50$  mm. To solve this problem VUV collimated photo-reactors in a  $\text{N}_2$  atmosphere have been recently reported [38,39]. This study reports for the first time in a detailed, systematic and comprehensive way the effect of 185/254 nm mercury resonance lines and separately the effect of the 185 nm line on the photo-Fenton mediated MB degradation in solution. This allows reporting the effect due to the radical species and the MB degradation induced by water VUV photolysis in a specific way compared to the effects of the 254 nm light in photo-Fenton mediated processes. The objective of the present study is to design and test the performance of improved AOP's technologies for water and wastewater treatment.

## 2. Experimental

### 2.1. VUV/UV photo-reactor reactor

The micro VUV/UV photo-reactor (length of 300 mm) [37] with double-layers-wall as shown in Supplementary material S1 was used throughout this study. The lamp was cooled by de-ionized water flow through the volume between double-layers-wall and the lamp housing to maintain constant lamp output. The 8W cold-cathode LP-UV synthetic quartz (arc length = 200 mm, from Haining Xiashi Co., Haining, China) emitted both 185 and 254 nm UV mercury resonance lines to obtain a uniform FR spatial distribution in the axial direction. Synthetic quartz tube was used in the photo-reactor transparent to the 185/254 nm light. A Ti-doped silica tube was used for the 254 nm light experiments. The inner diameter and length of both two tubes were 2 mm and 100 mm, respectively. Nearly same UV fluence rate (FR) could be obtained in the VUV/UV and UV tubes because both tubes presented a very high 254 nm transmittance. To obtain a uniform FR spatial distribution, two tubes were placed in the central region in the axial direction of the lamp avoiding the end-lamp regions (i.e., last 50 mm at each end of the lamp arc) where the FR distribution was observed not to be uniform. Nitrogen was flushed through the inner chamber of the reactor, to eliminate the air-absorption (e.g.,  $\text{O}_2$ ) and maximize the VUV reaching the samples.

### 2.2. Chemicals and analytical methods

Chemicals used for experiments were reagent grade or higher, supplied by Sigma-Aldrich or Fluka. Photo-Fenton experiments were carried out employing ferric chloride ( $\text{FeCl}_3$ ) and hydrogen peroxide (35% by weight). The  $\text{H}_2\text{O}_2$  concentration during this study was determined by the Titanium (IV) oxy-sulfate ( $\text{TiOSO}_4$  Fluka) method described in Ref. [40].

The MB concentration was determined spectrophotometrically following the peak at 664 nm. The 1,4-benzoquinone (BQ) and *tert*-butanol (TBA)[2,3,10] were used as the superoxide  $\text{O}_2^{\bullet-}$  and  $\bullet\text{OH}$  scavengers, respectively. Milli-Q water (Millipore) was used in all experiments and analytical determinations.

### 2.3. Experimental procedures

The experimental set-up was stabilized for 15 min prior to the re-circulation of the 50 ml sample in the photo-reactor. The peak of

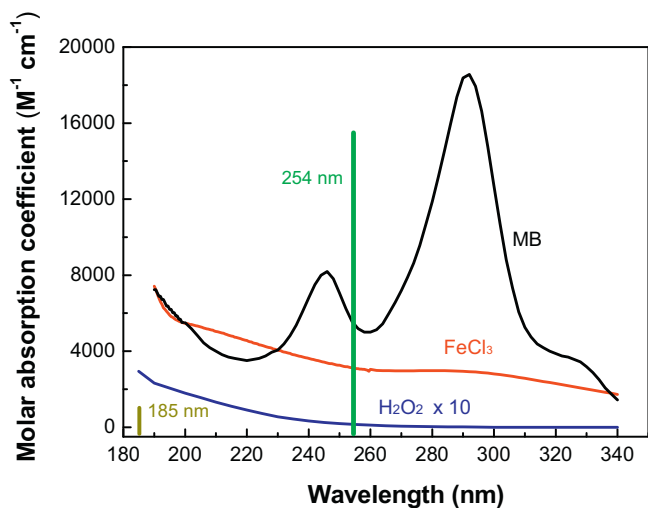


Fig. 1. The absorption spectra of  $\text{H}_2\text{O}_2$ ,  $\text{FeCl}_3$ , and MB and the mercury resonance lines at 254 nm and 185 nm of the VUV/UV low pressure mercury lamp used throughout this study.

MB as monitored by a UV1800, Shimadzu Co., Japan spectrophotometer until the desired exposure fluence was reached.  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  were used to adjust the initial pH before the degradation runs. The UV-vis spectrophotometer was used to carry out the on line analysis of the absorbing species at pre-selected time intervals of 0.5 min. The samples were collected for further analysis (e.g., methanol) and analyzed by gas chromatography in the flame ionization detector.

Uridine (0.12 mM) [40] and methanol (0.1 mM) [41] were both used in the actinometry for the determination of the UV fluence (FUV) as a function of time. Details are described in Supplementary material S2. In the VUV/UV tube, methanol could measure the VUV (185 nm) fluence directly, since its UV photolysis (at 254 nm) was low (Supplementary material S3). Therefore, the total fluence in the VUV/UV tube was similar to the sum of FUV and FVUV, since 99% of the VUV/UV mercury emission lines in the UV region were at 254 nm and at 185 nm. Likewise, the total fluence in the UV tube was approximately equal to FUV, since the 185 nm photons were completely absorbed by the  $\text{TiO}_2$ -doped tube wall. In addition, in the VUV/UV tube, the exposed fluence ratio of UV (254 nm) to VUV (185 nm) was determined to be 9.2, which was similar to the ratio provided by the manufacturer of the low pressure (LP) mercury lamps.

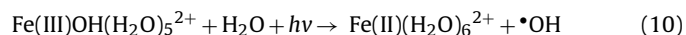
### 3. Results and discussion

#### 3.1. Basic considerations on photo-Fenton mediated reactions activated by UV and VUV light leading to MB degradation

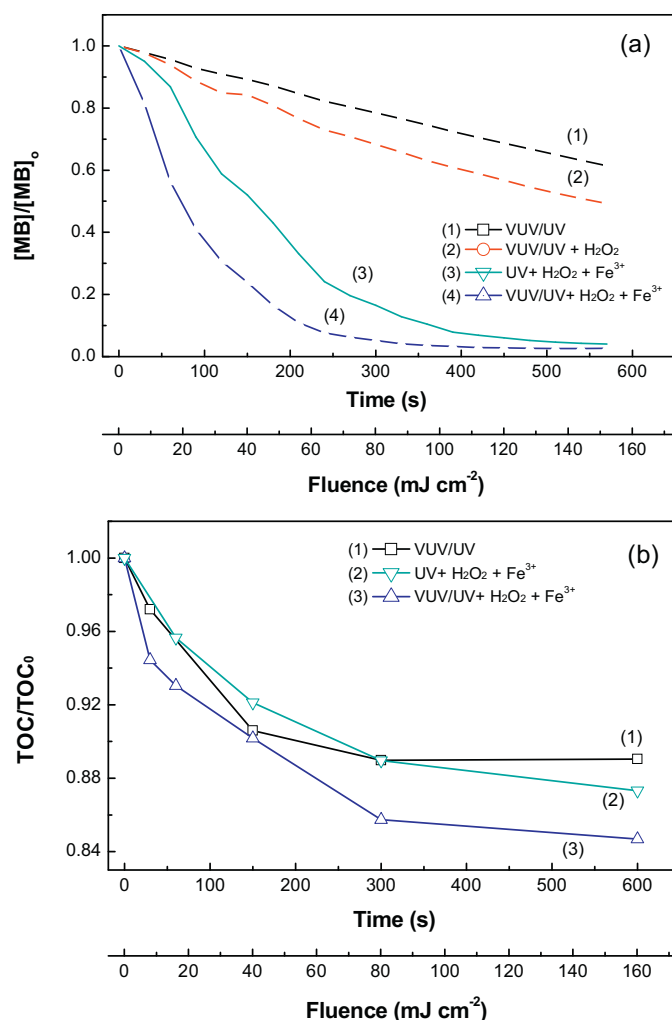
Fig. 2a shows the MB degradation by VUV/UV, UV/UV photo-Fenton and UV photo-Fenton processes at an initial pH 3.3. The VUV/UV in the absence of  $\text{H}_2\text{O}_2$  discolors the MB due to the radicals derived from the air ( $\text{O}_2$ ) present [28–35]. Eqs. (7)–(8) also show that OH-radicals generated by water photolysis may also intervene in MB-degradation. The contribution of  $\text{H}_2\text{O}_2$  will under irradiation by the 185/254 nm mercury resonance lines be higher compared to the 185 nm mercury resonance-line. But the light absorbed by  $\text{H}_2\text{O}_2$  in the UV and VUV/UV region is too small to have an important effect on MB degradation at the very low  $\text{H}_2\text{O}_2$  concentrations of 0.147 mM used in this study. The low molar absorption coefficients  $\text{H}_2\text{O}_2$ , low  $\text{H}_2\text{O}_2$  concentrations and the low photonic fluence associated with both mercury resonance lines may be responsible for this. The  $\text{H}_2\text{O}_2$  decomposition under light irradiation in the UV-region is shown by Eq. (9) [22–24].



Photo-Fenton UV/ $\text{H}_2\text{O}_2$ / $\text{Fe}^{3+}$  reactions led to a complete MB degradation within about 8 min under UV light as shown Fig. 2a. The photochemical behavior of the  $\text{Fe(III)-aqua}$  hydroxy-complexes plays a determining role in the  $\text{Fe-aqua}$  complex absorption [36,42,43]. The pH and molar extinction coefficient of these  $\text{Fe-aqua}$  complexes play a determinant role in the photo-Fenton reactions mentioned before Eqs. (1)–(6). At pH above 3, the  $\text{Fe(H}_2\text{O)}_6^{3+}$  is transformed into  $\text{Fe(III)OH(H}_2\text{O)}_5^{2+}$ , which is able to undergo ligand-to-metal-charge-transfer (LMCT). This treaction depends on the excitation wavelength and involves an inner sphere photo-induced electron transfer (LCMT) leading to  $\text{Fe(II)-aqua}$  complex and  $\cdot\text{OH}$  radicals through the reaction [44].



When  $\text{H}_2\text{O}_2$  is added to the MB solution under UV and VUV/UV light as shown in Fig. 2a, the higher efficiency of MB degradation can be explained by the  $\text{Fe(II)/Fe(III)}$  inter-conversion due to the MB-radicals produced during the MB degradation. This leads to an increased  $\cdot\text{OH}$ -radical production [15,45]. The experiments



**Fig. 2.** Methylene blue (MB) degradation (a) and TOC reduction (b) in different photo-Fenton processes. Conditions:  $[\text{MB}]_0 = 0.016 \text{ mM}$ ,  $[\text{H}_2\text{O}_2]_0 = 0.147 \text{ mM}$ ,  $[\text{Fe}^{3+}]_0 = 0.05 \text{ mM}$ , and  $\text{pH}_0 = 3.3$ . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

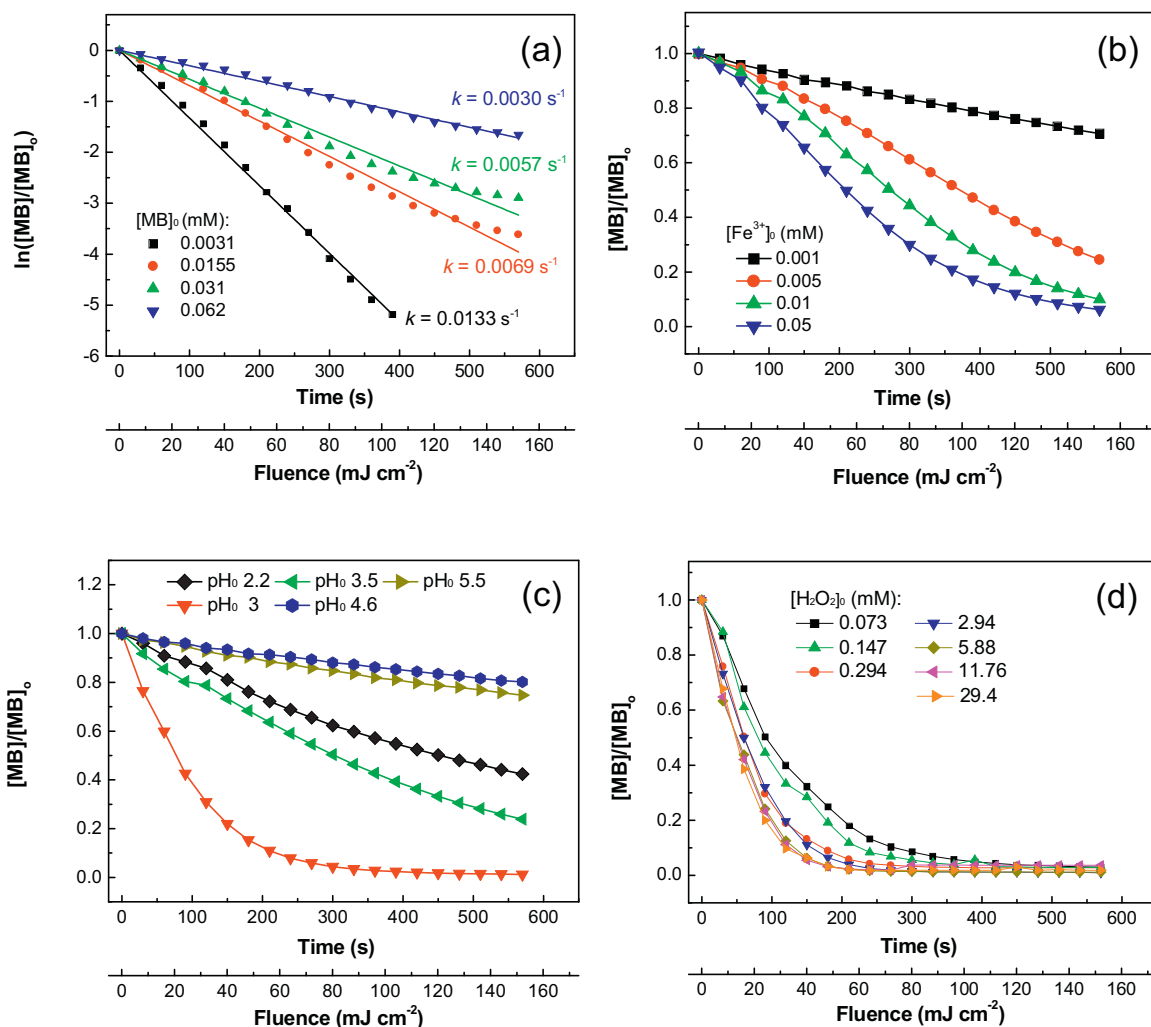
reported in Fig. 2a have been carried out in the presence of air ( $\text{O}_2$ ). The  $\text{Fe(III)OH(H}_2\text{O)}_5^{2+}$  reacts with the  $\text{O}_2$  in the photo-reactor leading to  $\text{O}_2^{\cdot-}$  radicals enhancing further MB degradation since  $\text{O}_2$  has been shown to be favorable [46,47] to Fenton/Photo-Fenton reactions.

Fig. 2b presents the mineralization of the MB under different experimental conditions up to 10 min. It is readily seen that the MB-mineralization to  $\text{CO}_2$  attains only ~15% after 10 min. This suggests that the MB degradation (Fig. 2a) lead mainly to long-lived intermediates. These results agree with results reported earlier by Herrmann during the photocatalytic discoloration of MB on  $\text{TiO}_2$  [48].

#### 3.2. Effects of the solution components on the kinetics of MB degradation: mechanistic considerations

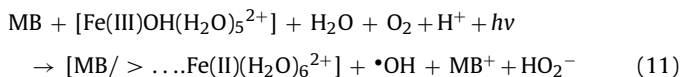
##### 3.2.1. MB degradation induced by VUV/UV and UV light

Fig. 3a shows the MB degradation as a function of the initial dye concentrations from 0.0031 to 0.062 mM. The results demonstrate that high concentrations of MB slow down the degradation kinetics, due to the competition for the limited number of oxidative radicals in solution. MB degradation will also be induced by the direct photolysis by light at 185/254 nm as shown previously in Fig. 2a. Table 1 shows that in the reaction solution ( $[\text{MB}]_0 = 0.016 \text{ mM}$ ,



**Fig. 3.** Effects of the initial concentrations of MB (a), Fe<sup>3+</sup> (b) and H<sub>2</sub>O<sub>2</sub> (c), and the initial pH (d) on MB degradation. (a) MB 0.0031 mM (*k* 0.0138); MB 0.0155 mM (*k* 0.069); MB mM 0.031 (0.0057); MB mM 0.062 (0.0030).

[H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 0.147 mM, [Fe<sup>3+</sup>]<sub>0</sub> = 0.05 mM), the photons absorbed by MB from the 185 nm light amounted to 5% and 29.8% from the 254 nm second resonance line. The overall MB degradation under VUV/UV light involves the redox reaction shown below in Eq. (11). The initial photo-induced MB<sup>\*</sup> formation is followed by its decomposition within short times [4,10,24,50]. For this reason we address in section 3.3 the scavenging of the •OH/HO<sub>2</sub>• radicals, to sort out the participation of these highly oxidative radicals during MB degradation.



The MB<sup>\*</sup> excited state has been reported to be a singlet with a lifetime of 358 ps intercrossing subsequently to the triplet state with a lifetime of 4.5 ms [48,49]. A diluted MB aqueous solution contains an O<sub>2</sub> concentration is  $0.5 \times 10^{-3}$  M. The probability of the triplet MB<sup>\*</sup> deactivation has been reported to be 0.04 [50]. The probability for the collision-controlled deactivation of MB<sup>\*</sup> by O<sub>2</sub> has been reported to be 0.53 [50]. The mechanism of the light induced MB degradation has been extensively reported and will not be discussed further in this study [51,52].

### 3.2.2. Effect of the Fe-ions optical band absorption added in solution

The runs reported in Fig. 3b were carried out at pH 3.3. At this pH the short-hand notation of the predominating species is

**Table 1**  
Reactant concentrations, molar absorption coefficients (ε), absorbance (A), and photon distribution percentage (P) at 254 and 185 nm in the VUV/UV micro photo-reactor.

Reactant	C (mM)	ε <sub>254</sub> (M <sup>-1</sup> cm <sup>-1</sup> )	ε <sub>185</sub> (M <sup>-1</sup> cm <sup>-1</sup> )	A <sub>254</sub>	A <sub>185</sub>	P <sub>254</sub> (%)	P <sub>185</sub> (%)
H <sub>2</sub> O	55.56	0.01	10	0.010	0.360	16.8	78.3
H <sub>2</sub> O <sub>2</sub>	0.147	19	341	0.001	0.010	0.9	2.2
FeCl <sub>3</sub>	0.05	3140	7250	0.031	0.073	52.6	15.8
MB	0.016	5562	7229	0.018	0.023	29.8	5.0
Total						100	100



$\text{Fe(III)(OH)}^{2+}$  [42]. The complete species is noted as  $\text{Fe(H}_2\text{O)}_5\text{OH}^{2+}$ . Under light irradiation, this complex undergoes redox reactions leading to  $\bullet\text{OH}$ -radicals [11,53,54]:



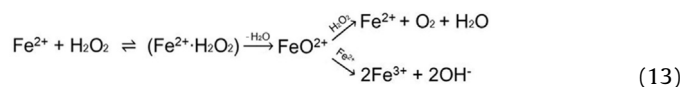
The most favorable MB photo-induced degradation was observed adding a concentration of 0.05 mM  $\text{Fe}^{3+}$  by Fig. 3b. The addition of  $\text{Fe}^{3+}$  to the MB-solution lead to a faster MB-degradation kinetics since more radicals are formed when more  $\text{Fe(III)}$  is present. The enhanced  $\text{H}_2\text{O}_2$  decomposition has been reported due to the increased concentration of the  $\text{Fe(III)-OO}^-$  species in solution [55,56]. The Supplementary material S4 provides information about the spectra of a 0.016 mM MB solution in the presence and absence of  $\text{FeCl}_3$ . This last reagent was used as the source of Fe-ions during this study. The  $\text{Cl}^-$  anions have a coordinating ability and will substitute water in the first coordination sphere of  $[\text{Fe(III)OH(H}_2\text{O)}_5]^{2+}$  yielding mixed ligand complexes such as  $\text{Fe(H}_2\text{O)}_5\text{Cl}^{2+}$  and  $\text{Fe(H}_2\text{O)}_4\text{Cl}^{2+}$  [57,58].

### 3.2.3. Effect of pH on the aqueous solution under VUV irradiation

The degradation of MB by VUV photo-Fenton processes at various pH's is shown in Fig. 3c. The kinetics presented in Fig. 3c confirms that the full hydrated  $\text{Fe}^{3+}$ -ion,  $\text{Fe(H}_2\text{O)}_6^{3+}$  is the most active catalytic species leading to the fastest MB degradation. When this aqua-metal complex gets de-protonated at  $\text{pH} < 3$ , it slows down the MB decomposition kinetics. At  $\text{pH} > 3$  due, the formation of hydroxylated Fe-complexes up to pH 4.6 also slow down the MB degradation. At  $\text{pH} \sim 4.6$  the  $\text{Fe(OH)}_3$  precipitates, and slows down the degradation of MB. But the slow MB-degradation involves hydrated Fe-hydroxide species present on the surface of the  $\text{Fe(OH)}_3$  precipitate.

### 3.2.4. Effect of the added $\text{H}_2\text{O}_2$ concentration

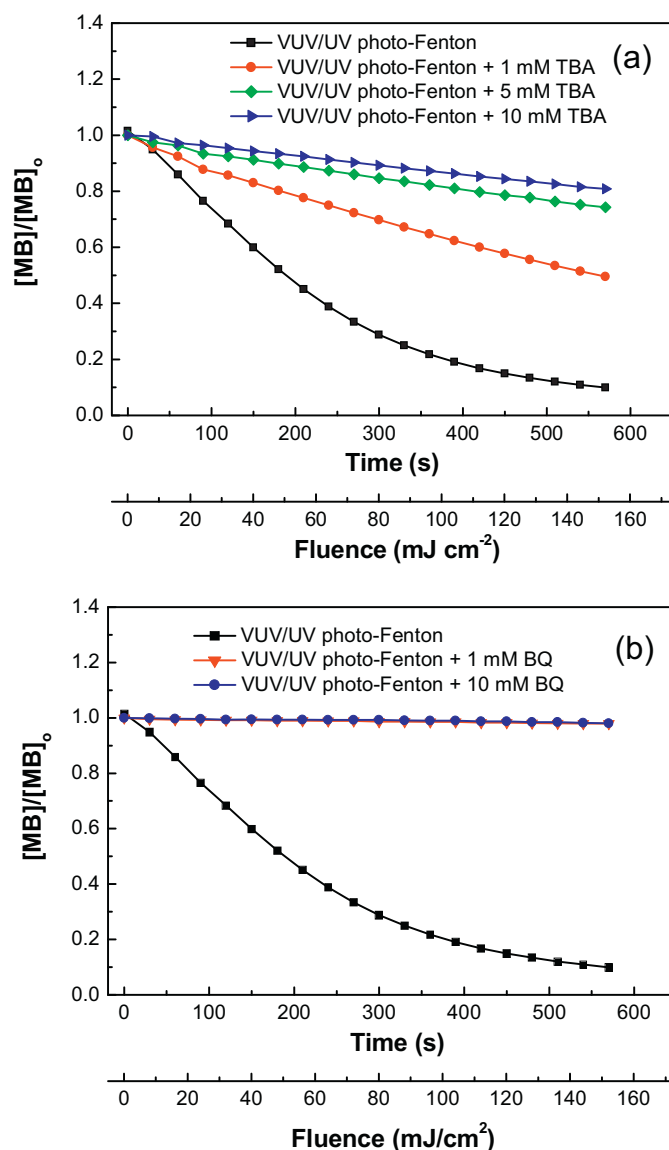
The MB degradation kinetics in Fig. 3d is shown to be almost insensitive to the concentration of  $\text{H}_2\text{O}_2$  added in solution. The MB degradation rate increased slightly upon  $\text{H}_2\text{O}_2$  addition from 0.073 to 5.88 mM under VUV in a solution with an initial pH 3.3. At  $\text{H}_2\text{O}_2$  concentrations between the 5.88 and 29.4 mM, the MB degradation was seen to be independent of the added  $\text{H}_2\text{O}_2$ . The excessive  $\text{H}_2\text{O}_2$  added in solutions scavenged the  $\bullet\text{OH}$  radical in solution [4,5]. During photo-Fenton reactions, the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  with a concomitant evolution of  $\text{O}_2$  has been reported [21]. Eq. (13) shows the redox processes in which  $\text{H}_2\text{O}_2$  is oxidized to  $\text{O}_2$  through a  $\text{FeO}^{2+}$  intermediate, occurs concomitantly with the  $\text{FeO}^{2+}$  species reacting with  $\text{Fe}^{2+}$  reducing  $\text{H}_2\text{O}_2$  to  $\text{OH}^-$



### 3.3. Scavenging of the main species leading to MB degradation

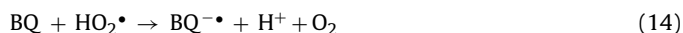
Fig. 4a shows the MB degradation for a solution by adding various concentration of *tert*-butanol (TBA). A reaction rate of  $1.9 \times 10^9$  has been reported for the reaction of TBA with the  $\bullet\text{OH}$ -radicals as determined by competition kinetics [37,44]. Fig. 4a shows that an increasing the concentration of TBA from 1 mM to 10 mM, led to a MB degradation decreased due to the quenching of the  $\bullet\text{OH}$  radicals by TBA [4,10,19].

Fig. 4b reports the MB-degradation in solution in the presence of benzoquinone (BQ), a well-known superoxide radical quencher via fast electron transfer [59–61]. Fig. 4b shows that the degradation of MB was completely inhibited by 1 mM BQ. This shows the most active species intervening in MB degradation is  $\text{HO}_2\bullet$ . BQ scav-



**Fig. 4.** MB degradation in the presence and absence of *tert*-butanol (TBA) (a) and benzoquinone (BQ) (b) under VUV/UV light irradiation. Conditions:  $[\text{MB}]_0 = 0.016 \text{ mM}$ ,  $[\text{H}_2\text{O}_2]_0 = 0.147 \text{ mM}$ ,  $[\text{Fe}^{3+}]_0 = 0.05 \text{ mM}$ , and  $\text{pH}_0 = 3.3$ .

enges the  $\text{HO}_2\bullet$  radicals with a bimolecular rate of  $9.6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$  leading to the formation of  $\text{O}_2$  noted below in Eq. (14) [61]:

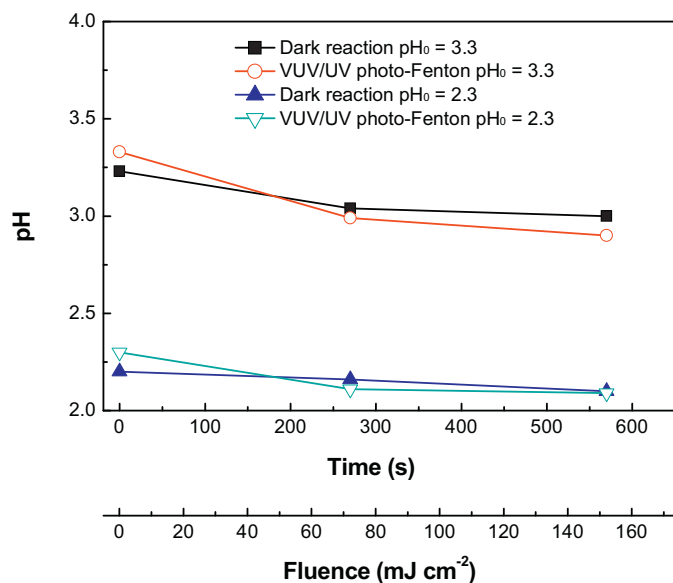


The  $\text{HO}_2\bullet$  radicals disproportionate at  $\text{pH} > 4.8$  as shown in Eq. (15):



Estimation of the  $\bullet\text{OH}$  radical lifetime takes into account the rate of the reaction  $\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \bullet\text{OH}$  ( $k_1 = 40\text{--}60 \text{ M}^{-1}\text{s}^{-1}$ ) and also of the reaction of  $\bullet\text{OH} + \text{MB} (\text{RH}) \rightarrow \text{products}$  ( $k_2 \sim 10^{10} \text{ M}^{-1}\text{s}^{-1}$ ). Inserting the solution parameters  $\text{MB} = 0.016 \text{ mM}$ ,  $\text{H}_2\text{O}_2 = 0.147 \text{ mM}$ ,  $\text{Fe}^{3+} = 0.05 \text{ mM}$  in the quasi-stationary state for  $\bullet\text{OH}$  concentration and approximating the radical concentration to zero (since it is almost negligible), renders a lifetime for the  $\bullet\text{OH}$  radical  $\sim 2 \text{ ns}$  (see Supplementary material S4).

To estimate the  $\text{HO}_2\bullet$  radical lifetime, the Eqs:  $\text{Fe}^{2+} + \text{HO}_2\bullet \rightarrow \text{Fe}^{3+} + \text{HO}_2^-$ ,  $k_3 = 8 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$  [15] and  $\text{HO}_2\bullet + \text{RH} (\text{MB}) \rightarrow \text{product}$   $k_4 \sim 1.2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$  were considered



**Fig. 5.** pH variations during the VUV/UV photo-Fenton and dark-Fenton processes at initial pH values of 2.3 and 3.3. Conditions:  $[MB]_0 = 0.016$  mM,  $[H_2O_2]_0 = 0.147$  mM,  $[Fe^{3+}]_0 = 0.05$  mM.

and allows to estimate a lifetime of 0.38 s for the  $HO_2^\bullet$  radical. The  $OH/OH^-$  potential 1.90 eV [62] is higher than the potential of  $\cdot HO_2/HO_2^-$  of 0.75 eV [63–65]. The Smoluchowski simplified approximation was used to calculate the mean-free path of the  $\cdot OH$ ,  $x_2 \cong D_T$  where  $D$  is the diffusion of molecules with a low molecular weight and  $T$  is the inverse of the pair  $MB + \cdot OH$  lifetime. Inserting the inverse of the reaction rate  $10^{10} M^{-1}s^{-1}$  and the MB concentration (i.e.,  $0.016 \times 10^{-3} M$ ) a mean-free path  $x \cong 52$  nm can be estimated for  $\cdot OH$ . By the same approach, a mean-free path for the  $HO_2^\bullet$  radicals of about 580  $\mu$  was estimated (see S6). The data in Fig. 4a and b, to suggest that the MB degradation is not controlled by the radical redox-potentials but by the radical lifetimes and mean-free diffusion distances.

#### 3.4. pH shift and pH dependent intervention of the $HO_2^\bullet$ radical during MB degradation

Fig. 5 shows that for a solution ( $[MB] = 0.016$  mM,  $[H_2O_2] = 0.147$  mM,  $[Fe^{3+}] = 0.05$  mM, at an initial pH = 3.3, the pH moves to more acidic values in the dark and under VUV/UV irradiation during MB degradation as suggested in Eq. (16). The pH shift in the solution under VUV/UV from 3.3 to 2.8 shown in Fig. 5 corresponds to a fourfold increase in the  $H^+$  concentration in solution. This pH shift is due to: (a) the  $MB^+$  acid-cation generation noted in Eq. (11), and (b) the build up of short carboxylic long-lived acid intermediates in solution containing COOH groups with  $pK_a$  values  $\sim 3.0$  as reported by Herrmann et al. [48]. The shift to more acid values during the MB-degradation time is suggested in Eq. (16)

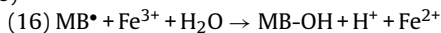
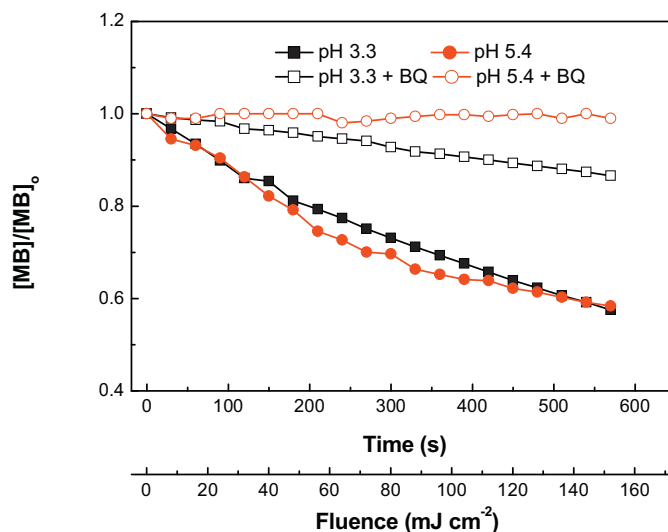
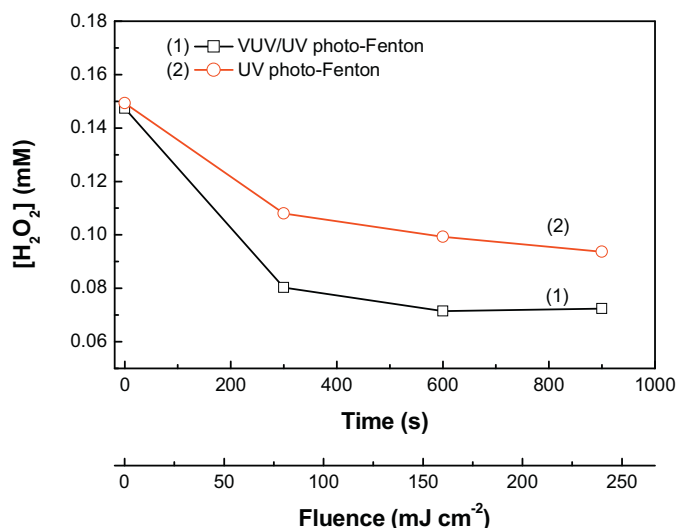


Fig. 6 shows MB degradation by VUV/UV/ $H_2O_2$  ( $H_2O_2$  0.147 mM) process in the presence and absence of BQ at pH values of 3.3 and 5.4. In the dark (full points) BQ did not preclude MB-degradation since no radicals were produced. This is not surprising due to the fact that the oxidation of organic compounds by  $H_2O_2$  in the dark have been reported to be independent of pH [66,67]. But under VUV/UV light, the  $H_2O_2$  at pH 3.3 leads to  $HO_2^\bullet$ . In this case Fig. 6 shows that only about 12% MB was degraded within 10 min. The data at pH 5.4 for light activated MB-degradation shows that no MB degradation was observed at this pH. The reason for this



**Fig. 6.** MB degradation by VUV/UV/ $H_2O_2$  in the presence and absence of BQ at initial pH values of 3.3 and 5.4. Conditions:  $[MB]_0 = 0.016$  mM,  $[H_2O_2]_0 = 0.147$  mM.



**Fig. 7.** Change of  $H_2O_2$  concentration with reaction time during the VUV/UV and UV photo-Fenton processes. Conditions:  $[MB]_0 = 0.016$  mM,  $[H_2O_2]_0 = 0.147$  mM,  $[Fe^{3+}]_0 = 0.05$  mM, and pH 3.3.

observation is that at pH 5.4, the  $HO_2^\bullet$  radicals disproportionate to  $O_2^{\cdot -}$  as shown previously in Eq. (15).

#### 3.5. $H_2O_2$ consumption during MB degradation as a function of the applied light

Fig. 7 shows the decrease of the initial concentration of  $H_2O_2$  during VUV/UV photo-Fenton and UV photo-Fenton processes. The former shows a more rapid decrease of  $H_2O_2$  concentration, due to the higher light dose. The  $H_2O_2$  decrease in UV photo-Fenton process is slower when applying only 254 nm light because the molar absorption coefficient of  $H_2O_2$  at 254 nm  $19 M^{-1}cm^{-1}$  is low and the fluence is also not high ( $300 mJ cm^{-2}$ ).

Generation of  $H_2O_2$  during VUV/UV photolysis has been reported in the presence of dissolved  $O_2$  and organic compounds in solution [30,34,35]. The mechanism involves  $H^\bullet$  trapping by  $O_2$  yielding  $HO_2^\bullet$ . These radicals subsequently recombine to yield  $H_2O_2$ . About 0.025 mM  $H_2O_2$  was generated in pure  $H_2O$  under VUV/UV (see Supplementary material S7). However, during the MB

degradation by VUV/UV photo-Fenton the amount of  $\text{H}_2\text{O}_2$  generated by VUV/UV is much lower compared to the added initial  $\text{H}_2\text{O}_2$  concentration of 0.147 mM.

#### 4. Conclusions

The discoloration/degradation of MB by the Fenton reagent was enhanced by VUV/UV and UV irradiation from low-pressure mercury lamps. The effects of the initial MB,  $\text{Fe}^{3+}$  and  $\text{H}_2\text{O}_2$  concentrations were evaluated as well as the effect of the initial pH during the MB degradation. The effect of the  $\text{HO}_2$ -radical scavenging at different pH and their effect on the MB degradation kinetics was discussed. Appropriate radical scavengers identified the main oxidative radicals leading to MB degradation. The radical lifetimes and their diffusion distances in aqueous solution were estimated. A simplified mechanism for the radical species leading to MB oxidation is suggested in this study.

#### Acknowledgments

This work was supported by: the National Natural Science Foundation of China (51408592) and Marie Curie/E.U. Seventh Program FP7/2007–2013 under the REA (Agreement No. 318926), the EPFL and COST MP1106.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2016.01.014>.

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